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## **Progress Report - July 31, 1996**

### **NASA Grant # NCC-1-214**

#### **Interpretation of Lidar and Satellite Data Sets using a Global Photochemical Model**

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## 1. Accomplishments

The status in the beginning of the report period was that the existing General Circulation Model (GCM) was running with a chemistry module compiled for stratospheric simulation studies. The chemistry simulation was not working sufficiently in the troposphere and any tropospheric trace gas sources or dry deposition sinks were not yet incorporated.

The current status concerning the chemistry module is that

- the chemistry simulation has been modified to also simulate the chemistry in the troposphere with resulting mixing ratios close to other model simulations as described in Olson et al. (1996).
- The mechanism to incorporate trace gas source, e.g. testing for  $\text{NO}_x$ , and dry deposition sinks, testing for  $\text{H}_2\text{O}_2$ ,  $\text{CH}_3\text{OOH}$ ,  $\text{O}_3$ ,  $\text{HCHO}$ ,  $\text{HNO}_3$ , and  $\text{NO}_2$ , are incorporated and is currently being tested.

Existing model and development versions:

- The full GCM model, currently still running with the original stratospheric chemistry module.
- An off-line version of the GCM, i.e. wind and photolysis rates are pre-calculated and prescribed in read-in arrays. Here, the current modification are incorporated and are under test.
- A box model version of the modified chemistry module for developments and first tests of new modifications.
- A box model with same chemistry simulated but flexible partitioning and integration methods for test purposes of those.

Several NASA scientist working in a joint effort on the development of the GCM at the NASA Langley Research Center which is funded through different grants. In particular three scientists, including the grantee, are working on the tropospheric chemistry part. Consequently the entire tropospheric development was not accomplished by the grantee alone. The grantee's work focused mainly on three areas:

- Trace gas sources and dry deposition
- Method to introduce a NO source instead of a  $\text{NO}_x$  source
- Investigating integration methods

These three areas and accomplishments are discussed in more detail:

- Tropospheric chemistry, dry deposition and trace gas sources

A mechanism for computing trace gas production and loss terms caused by trace gas source and dry deposition fields has been incorporated in the off-line GCM version and is in a test phase.

*Mechanism:* The calculation of deposition and source terms is using prescribed deposition velocity (currently for O<sub>3</sub>, HCHO, H<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>OOH, NO<sub>2</sub>, and HNO<sub>3</sub>) and source flux arrays (currently for NO<sub>x</sub>). Deposition velocities (or the associated transport resistance, see below) and source fluxes are the form in which, in general, the data are available in literature.

The deposition velocity ( $v_{dep}$ ) is defined as (Warneck 1990)

$$v_{dep} = 1 / (R_g + R_s)$$

where  $R_g$  and  $R_s$  are the ground and surface resistance, respectively, using the assumption that the surface flux is equal to the ground flux.  $R_g$  reflects the transport resistance in the lowest few centimeters adjacent to a surface, and  $R_s$  is surface specific, e.g. surface could be bare ground or leaves. Deposition velocities are species and surface specific. In this test phase values from Müller (1992) for O<sub>3</sub>, HCHO, H<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>OOH, and HNO<sub>3</sub> are used. The velocities for the different species are assigned to different vegetation classes. An longitude-latitude array has been generated using the NCAR vegetation database ds.769 overlaid with snow and ice data used in the GCM. The resulting data array groups the earth surface into seven classes: ice/snow, water, bare ground, grass/shrubs, grass/shrubs/trees, non-tropical forest, and tropical forest (Figure 3) on a 0.5x0.5 degree resolution. The deposition velocities are assigned to this database and then averaged to the 128x64 model grid array. Resulting deposition arrays for HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and O<sub>3</sub> are shown in Figure 4a-c.

An additional transport resistance has to be introduced for the model surface interface, i.e. the column between surface and lowest model layer, in order to scale the deposition velocity which is defined at ground level ( $v_{dep}$ ) to a deposition velocity ( $v_{dep}^*$ ) at the lowest model layer. This surface interface resistance  $R_d$  is the inverse of the model air/surface interaction coefficient  $D_r$  (Model description; Stull 1988):

$$R_d = 1 / D_r = 1 / (C_d * M)$$

where  $C_d$  and  $M$  are the drag coefficient and a mean wind velocity, respectively.  $v_{dep}^*$  is then (e.g. Levy et al. 1985)

$$v_{dep}^* = 1 / (R_s + R_g + R_d) = v_{dep} \times (1 - v_{dep} / D_r)$$

$D_r$ , i.e.  $C_d$  and  $M$ , arrays will be provided from the transport routine of the model in order to calculate the modified deposition velocity  $v_{dep}^*$  and associated loss rate in the chemistry routine.  $M$  is differently calculated for stable and unstable planetary boundary layers. Currently, for  $D_r$  is assumed some global averaged number for the off-line test version of the model.

The conversion of deposition velocities and sources fluxes into loss and production terms is performed as

$$L_{dep}[1 / \text{sec}] = v_{dep} * (dz / 2)$$

$$P_{src}[\text{molec} / \text{cm}^3 / \text{sec}] = F_{surface} / (dz / 2)$$

$$P_{src}[\text{molec} / \text{cm}^3 / \text{sec}] = F_{cell} / dz$$

where  $dz$  is the thickness of the model layer. For fluxes and losses from/to the ground surface one has to use the column height between ground and the actual height of the layer center, that is  $dz/2$ , where the model calculations are performed. For sources generated inside a certain cell volume not originating from the surface, like the NO source from lightning or aircraft emissions, the thickness of the entire layer  $dz$  has to be used. As example, the difference between one-day model runs with and without deposition is shown for the resulting  $\text{H}_2\text{O}_2$  and  $\text{O}_3$  mixing ratios in the lowest model layer in Figure 5. As expected from the deposition velocity arrays (compare Figure 4), the major losses appear over land and water and over land for  $\text{H}_2\text{O}_2$  and  $\text{O}_3$ , respectively.

*Status:* The  $\text{NO}_x$  source and deposition terms added to the off-line GCM version are still under test.

- A method to introduce NO sources instead of  $\text{NO}_x$  sources to the chemical routine.

*Problem:* Since combustion processes emit mostly NO it would be more appropriate to introduce an  $\text{NO}_x$  source in form of NO into a chemical model simulation. During daytime, NO is oxidized to  $\text{NO}_2$  and  $\text{NO}_3$  and rapidly recycled to NO through photolytic decomposition of  $\text{NO}_2$  and  $\text{NO}_3$  forming a catalytic chain reaction. Especially in the limit of nighttime conditions, i.e. under missing photolytic decomposition of  $\text{NO}_3$  to  $\text{NO}_2$  and  $\text{NO}_2$  to NO, introducing  $\text{NO}_x$  in form of  $\text{NO}_2$  instead of NO would miss the oxidation step  $\text{NO} + \text{O}_3$  and its associated loss rates for ozone. In the limit of daytime conditions it makes primarily no difference of adding either  $\text{NO}_2$  or NO because the catalytic NO- $\text{NO}_2$  cycle has a very high gain (chain length) in the order of several hundred recycles before NO/ $\text{NO}_2$  is lost into long lived reservoirs like  $\text{HNO}_3$ ,  $\text{HNO}_4$ , or PAN, and the difference of transitions  $\text{NO} \rightarrow \text{NO}_2$  and  $\text{NO}_2 \rightarrow \text{NO}$  can only be maximal one of total hundreds per added NO or  $\text{NO}_2$ . The transition between day and nighttime conditions is more complicated while the chain length of the NO/ $\text{NO}_2$  catalytic cycle drops to zero and the oxidation to  $\text{NO}_3$  and the loss to  $\text{N}_2\text{O}_5$  increases. Nevertheless, since all these transitions are faster than tens of seconds and fast compared to integration time steps of typically  $dt \geq 900\text{s}$  for global or regional model simulations, the NO- $\text{NO}_2$ - $\text{NO}_3$  systems will be in photochemical equilibrium (PCE) and can be analyzed under fixed conditions, i.e. fixed mixing ratios resulting from the partitioning of  $\text{NO}_x$ , for a particular time  $t$ . A NO source cannot simply be added as NO to the chemical system because NO- $\text{NO}_2$  or  $\text{NO}_2$ - $\text{NO}_3$  already appear in PCE after partitioning and the fast relaxation processes, esp. in catalytic chains, cannot be resolved under a time step of  $dt$ .

**Method:** The chemical system is analyzed for a certain time  $t$ , this is no time step  $t_0 \rightarrow t_1$  is performed but the flow of chemical reaction paths is analyzed based on the branching ratios between competing reactions under fixed species concentrations. The total sum of a species loss or production from reactions inside a feedback loops, like  $\text{NO} \rightleftharpoons \text{NO}_2$ , can be parameterized in its loss or originating reaction times the gain (chain length) of the feedback loops. E.g. the loss of  $\text{O}_3$  from its reaction with  $\text{NO}$  ( $\text{LO}_3(\text{NO}+\text{O}_3)$ ) per initial  $\text{NO}$  molecule ( $\text{O}_3$  yield per  $\text{NO}$ ) can be written as the branching ratio of  $\text{NO}$  reacting with  $\text{O}_3$  against the sum of all possible  $\text{NO}$  reactions ( $\alpha_{\text{NO}+\text{O}_3}$ ) times the  $\text{NO} \rightleftharpoons \text{NO}_2$  loop gain  $G_{12}$  (indices 1 and 2 symbolize  $\text{NO}$  and  $\text{NO}_2$ ;  $G_{23}$  will be the loop gain of  $\text{NO}_2 \rightleftharpoons \text{NO}_3$ ), see Equ. 2. The lower of the indices of  $\text{LO}_3$  symbolizes its yield per initial molecule  $X$ , e.g.  $\text{NO}$ , and the upper one symbolizes the chemical system analyzed, e.g. here the  $\text{NO} \rightleftharpoons \text{NO}_2$

$$\text{LO}_3(\text{NO} + \text{O}_3) \Big|_{\text{NO}}^{\text{NO} \leftrightarrow \text{NO}_2} = G_{12} \times \alpha_{\text{NO}+\text{O}_3},$$

**Equ. 2**  $\text{O}_3$  loss per initial  $\text{NO}$  from  $\text{NO}+\text{O}_3$  inside the  $\text{NO} \rightleftharpoons \text{NO}_2$  catalytic chain loop.

$$\text{LO}_3(\text{NO} + \text{O}_3) \Big|_{\text{NO}_2}^{\text{NO} \leftrightarrow \text{NO}_2} = G_{12} \times \alpha_{j\text{NO}_2} \times \alpha_{\text{NO}+\text{O}_3}$$

**Equ. 1**  $\text{O}_3$  loss per initial  $\text{NO}_2$  from  $\text{NO}+\text{O}_3$  inside the  $\text{NO} \rightleftharpoons \text{NO}_2$  catalytic chain loop.

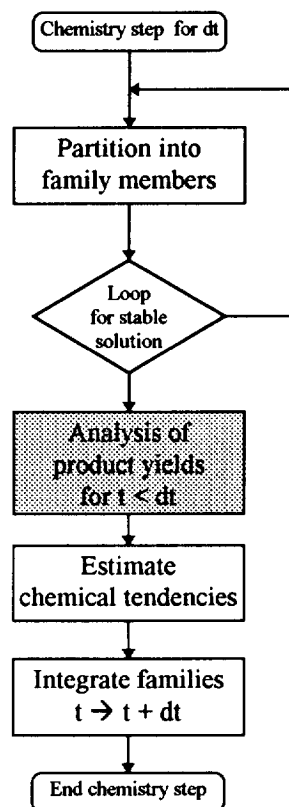
loop (no feedback from  $\text{NO}_3$  included). Equ. 1 shows the  $\text{O}_3$  loss of this reaction yielded per initial  $\text{NO}_2$ . During daytime, (and for not too high  $\text{O}_3$  concentrations)  $\alpha_{\text{NO}+\text{O}_3}$  and  $\alpha_{j\text{NO}_2}$  are close to one ( $>0.99$ ), thus  $\text{LO}_3$  either per initial  $\text{NO}$  or  $\text{NO}_2$  result in the same value, this is it makes primarily no difference adding  $\text{NO}$  or  $\text{NO}_2$  during daytime. It turns out that the entire  $\text{O}_3$  loss yield per initial molecule  $X$  ( $X=\text{NO}, \text{NO}_2, \dots$ ) can be parameterized into the form of Equ. 3.  $f$ ,  $g$ , and  $h$  are product terms of branching ratios  $\alpha$  describing the path from the initial molecule to the target reaction (e.g.  $\text{NO}+\text{O}_3$  or  $\text{NO}_2+\text{O}_3$ , see examples in Equ. 2 and Equ. 1), and  $G_{123}$  is an additional overall loop gain arising from the coupling of the two feedback loops  $\text{NO} \rightleftharpoons \text{NO}_2$  and  $\text{NO}_2 \rightleftharpoons \text{NO}_3$ .

$$\text{LO}_3 \Big|_X^{\text{NO} \leftrightarrow \text{NO}_2 \leftrightarrow \text{NO}_3} = G_{123} \times \left\{ G_{12} \times f_X(\alpha_i) + G_{23} \times g_X(\alpha_j) + G_{12} \times G_{23} \times h_X(\alpha_k) \right\}$$

**Equ. 3** Total  $\text{O}_3$  loss per initial  $X$  ( $X=\text{NO}, \text{NO}_2, \dots$ ) from the  $\text{NO} \rightleftharpoons \text{NO}_2 \rightleftharpoons \text{NO}_3$  coupled catalytic loops.

**Model incorporation:** The chemical routine (chemical solver) is initialized with mixing ratios of transported long lived families, i.e. groups of species, and the source flux arrays. The initial mixing ratio of a species family is then the result of chemical integration from the prior time step, plus the modification from transport calculations, plus an additional amount calculated from the source flux. The chemical solver can be seen separated in the partitioning of the long lived families into their shorter lived members, the estimation of chemical tendencies based on the chemical interaction of the partitioned species, i.e. computing of production and loss terms, and the final integration of the families (Figure 1). The partitioning step is in general iterated to gain stable solutions for, e.g. radicals like OH or NO while their production and loss terms depend strongly on each other.

The new approach introduces an additional subroutine which analyses product yields of processes fast compared to time step  $dt$ , particular in this case, the  $O_3$  yield of the NO-NO<sub>2</sub>-NO<sub>3</sub> catalytic cycle per NO or NO<sub>2</sub> added. This analysis would be placed after the partitioning (see Figure 1, shaded box). Here, the ratio  $RLO_3$  of the  $O_3$  loss yield per NO over the loss yield per NO<sub>x</sub> in PCE (i.e.  $NO/NO_x=a$ ,  $NO=aNO_x$ ,  $NO_2=(1-a)NO_x$ ) will be calculated (see Equ. 4b); NO<sub>x</sub> in PCE, this is the NO/NO<sub>2</sub> PCE ratio for daytime, and NO<sub>2</sub> for nighttime.  $RLO_3$  can be used to correct the loss term  $LO_3$  of the chemical tendency for  $O_3$  (see Equ. 4c) which will be, as usual, in a first step estimated for  $dt$  based on total NO<sub>x</sub> in PCE (see Equ. 4a). I.e. the fraction of  $LO_3$  originating from the NO source will be multiplied by  $RLO_3$ , gaining a final corrected chemical tendency for  $O_3$ .



**Figure 1.**

Chemical solver

$$NO_x^{tot} = NO_x^{init} + NO_x^{source}$$

$$RLO_3 = LO_3 \Big|_{NO}^{NO \leftrightarrow NO_2 \leftrightarrow NO_3} / LO_3 \Big|_{NO, inPCE}^{NO \leftrightarrow NO_2 \leftrightarrow NO_3}$$

$$LO_3(NO_x^{tot}, dt) = LO_3(NO_x^{tot}, dt) \times \left\{ \frac{NO_x^{init}}{NO_x^{tot}} + \frac{NO_x^{source}}{NO_x^{tot}} \times RLO_3 \right\}$$

**Equ. 4**

- a) total  $NO_x$  = initial  $NO_x$  (from prior time step) +  $NO_x$  source.
- b) Ratio of  $O_3$  loss yield per NO over yield per  $NO_x$  (in PCE) for the  $NO \leftrightarrow NO_2 \leftrightarrow NO_3$  catalytic chain loops.
- c) Correction of the loss term of the  $O_3$  tendency which has been calculated for dt and  $NO_x^{tot}$  which will correct the  $O_3$  loss yield for introducing a  $NO_x$  source in form of NO.

*Status:* To test Equ. 4.b,  $RLO_3$  has been calculated for mixing ratios of species compiled in box model runs initialized with 4 standard sets of species mixing ratios, altitude, and temperature: the 4 “IPCC cases” marine”, “land”, “plume-X”, and “free-troposphere” which were used for model inter-comparisons (Olson et al. 1996). Results are shown in Figure 6. As expected,  $RLO_3$  is equal to one for daytime.  $RLO_3$  significantly becomes >1 when the  $NO_3$  photolysis rate drops below 10% of its noon value. At nighttime there is no photolytic decomposition of  $NO_2$  and  $NO_3$  recycling NO ( $\rightarrow G_{12}=G_{23}=G_{123}=1$ ). Thus the maximum  $O_3$  loss per initial NO and  $NO_2$  is 2 and 1 (nominator and denominator of Equ. 4.b), respectively, through reactions  $NO+O_3$  and  $NO_2+O_3$ . Since  $NO_2+O_3$  is competing against  $NO_2+NO_3 \rightarrow N_2O_5$  the nominator and denominator of Equ. 4b will range between 1-2 and 0-1, resp. (neglecting  $NO+NO_3$ ), and  $RLO_3$  will become >2. The difference in amplitude of  $RLO_3$  between cases “land” and “marine” are due to different species mixing ratios, while the higher amplitude for “plume-X” and “free-troposphere” is due to lower temperatures and associated more favorable losses into the  $N_2O_5$  reservoir. Increasing  $RLO_3$  values during night are associated with increasing  $NO_3$  mixing ratios (not shown) causing increasing losses towards  $N_2O_5$ .

In a next step this needs to be added and tested in the off-line version of the GCM. Likely, this analytical method can also be used to calculate, e.g. OH,  $HO_2$ , or  $O_3$  yields from fast non-methan hydrocarbons (NMHC) reaction chains when adding NMHC chemistry to the model.

- Comparison of integration steps

Integration in the chemical solver using 900 second time steps show variations after a compared to 10 second fine step integration, e.g. after 5 days the differences for diurnal means can be in the order of 10% depending on initial conditions (IPCC cases). In the model version used for development, generally, for integration time step  $dt > 5\tau$  ( $\tau$  is lifetime of species X),  $0.2\tau < dt < 5\tau$ , and  $dt < 0.2\tau$  the integration over  $dt$  is calculated using photochemical equilibrium (PCE) assumption, implicit, and forward Euler integration

$$X(t_1) = (P - L \times X(t_0)) \times dt$$

$$X(t_1) = \frac{P \times dt + X(t_0)}{1 + L \times dt}$$

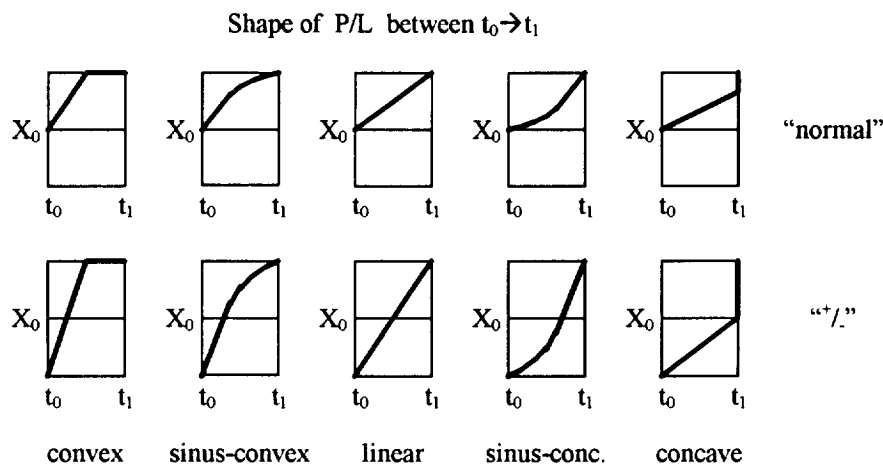
$$X(t_1) = X(t_0) + \left( \frac{P}{L} - X(t_0) \right) \times \exp(-L \times dt)$$

**Equ. 5** Integration steps: “forward Euler”, “implicit”, and “exponential”, respectively

steps, respectively (see Equ. 5). All are functions of the production (P) and loss (L) terms. For a chemical solver as shown in Figure 1 with an iteration loop for the partitioning section the resulting terms P and L are generated for the time  $t_0$ . The “correct” values for P and L would be some integral of P(t) and L(t) between  $t_0$  and  $t_1$  which is unknown since calculations are only performed for times in step of  $dt$ . It has been investigated how integration results vary if one uses P( $t_1$ ) and L( $t_1$ ) instead of P( $t_0$ ) and L( $t_0$ ) or some average of them. P and L for  $t_1$  can be calculated if one adds an additional iteration loop including the estimate of tendencies and the integration of families (compare Figure 1). The integration results for  $dt$  are compared to a fine step integration using forward Euler integration in steps of  $\tau/100$  which don’t differ anymore from results using even finer time steps and are assumed to be “correct” solution with error  $<<1\%$ . Different P/L shapes were assumed between  $t_0$  and  $t_1$  as illustrated in Figure 2. The envelopes of the resulting ratios between  $dt$  step integration and  $\tau/100$  step integration are shown in Figure 7-9 as function of  $\tau$ . Positive numbers in these graphs mean, the  $dt$  integration overestimates values for  $X(t_1)$ , while negative numbers indicate an underestimation. It turns out that forward Euler and implicit integration steps for the above defined time domains using P and L of  $t_0$  general underestimate any results while using P and L of  $t_1$  overestimate any results for  $X(t_1)$  (compare Figure 7, Figure 8). This general trend could also be verified in box model runs using these two possible sets of P and L values. Using an exponential integration step (this is the correct solution for a P/L shape stepping at  $t_0$  to its final values P/L( $t_1$ ) and staying constant over  $dt$  and only for this shape!) gives similar results as the implicit step with slightly smaller error for the implicit one (the results using the exponential step are not displayed). ( Note, that the large errors for the PCE values originate from concave shape calculations. A PCE state can hardly be reach if the change



of the  $P/L$  value increases in time. At some point the system cannot anymore follow the changing  $P/L$  value fast enough. )



**Figure 2** Shapes of (production)/(loss)= $P/L$  term steady state values assumed between integration time step  $t_0$  and  $t_1$ . In “normal” the species mixing ratio at  $t_0$  is at its equilibrium value  $P/L(t_0)$ , in “+/-” cases the  $P/L$  value crosses the start value  $X_0$ . Shapes with opposite signs (mirrored at  $y=X_0$ ) will just flip sign of integration results. Concave and sinus-concave cases reflect the situation after sunrise and after noon where  $P/L$  values generally change increasingly. Convex and sinus-convex cases reflect cases before noon and before sunset where changes in  $P/L$  decrease. Approximately linear changes

Figure 9 show the envelope of results choosing  $P=P(t_1)$  and  $L=L(t_1)$  for the linear and convex  $P/L$  shapes, and  $P=(P(t_0)+P(t_1))/2$  and  $L=(L(t_0)+L(t_1))/2$  for the concave shapes, additionally implicit steps are used for  $dt > 5\tau$  instead of PCE calculation in case of concave shapes. The error band indicated by the envelope curves is much smaller than for the calculation using either  $P$  and  $L$  only as function of  $t_0$  or  $t_1$ . A more sophisticated exponential integration step, consisting of three different exponential terms which are function of  $P(t_0)$ ,  $P(t_1)$ ,  $L(t_0)$ , and  $L(t_1)$  has been found which can compute results with much lesser errors than any other integration step discussed here. But two parameter have to be optimized for the specific shape of  $P/L$ .

The point is, one can possibly improve the performance of the integration step by using not only production and loss term ( $P$  and  $L$ ) as function of  $t_0$  but also of  $t_1$ , as discussed above. But one has to introduce the mentioned outer iteration loop in the chemical solver routine which would mean that more computing time is used. Additionally, one has to setup criteria that define for what time period (associated with different  $P/L$  shapes in time) which kind of averaged value of  $P$  and  $L$  need to be used (two different types might be sufficient). This might be possible but has not yet been tested thoroughly with the box model, and improvements could not be verified yet.

## **2. Comparison to proposed work**

The work proposed for the report period was mainly focused on preparing data arrays from field experiment, e.g. O<sub>3</sub> LIDAR data, and starting a data-model comparison. The status of the tropospheric part of the model in the beginning of this report period was far from starting reasonable comparisons, e.g. the at this time incorporated basic chemistry was optimized for the stratosphere requirements and needed to be modified to work in the troposphere, neither were surface source and sink (dry deposition) terms incorporated which are essential for global tropospheric simulations. It seemed therefor to be more important first to focus on the model development to reach a status of the model where reasonable data-model comparison could be started.

## **3. Milestones for the last grant year 08/96-07/97**

- Model development
  - \* Finalize testing of deposition and NO<sub>x</sub> source terms
  - \* Incorporate NO source instead of NO<sub>x</sub> source
  - \* Incorporate CO source and dry deposition, and also for hydrocarbons in time when associated chemistry will be incorporated.
  - \* Start to incorporate NMHC chemistry.
  - \* Look more into whether integration methods for chemical tendencies could be improved.
  - \* Develop and test above tools in off-line version and incorporate them in the full GCM version.
- Data-model comparison
  - \* Prepare software tools and data arrays to use TOMS residual ozone database and the LaRC ozone sonde database for climatological model evaluations. Start model evaluations
  - \* Build up database of regional/large scale experiments, e.g. TRACE-A/SAFARI-92 or PEM-West, for model comparison.
  - \* Use prescribed ECMWF or ECM wind fields with off-line GCM version for comparison with regional field data sets in specific time periods.

## Figure captions

**Figure 3.** Vegetation classes grouped using the NCAR Olson ds.769 vegetation database, 0.5x0.5 degrees (<http://www.ucar.edu/dss/datasets/ds769.0.html>) and snow/ice data used in the GCM.

**Figure 4.** Deposition velocity grid arrays for a)  $\text{HNO}_3$ , b)  $\text{H}_2\text{O}_2$ , and c)  $\text{O}_3$ .

**Figure 5.** Difference of a)  $\text{H}_2\text{O}_2$  AND b)  $\text{O}_3$  mixing ratios in the lowest layer between 1-day 3D model runs with and without deposition terms.

**Figure 6.** Correction factor  $\text{RLO}_3$  for correcting the  $\text{O}_3$  loss term for adding a  $\text{NO}_x$  source in form of  $\text{NO}$  instead of  $\text{NO}_x$ .  $\text{RLO}_3$  is calculated following Equ. 4b for the four “IPCC cases”. Additionally, the  $\text{NO}_2$  and  $\text{NO}_3$  photolysis rates are displayed.

**Figure 7.** Ratio of integration results as function of lifetime  $\tau$  of a species X. Used were  $P=P(t_0)$  and  $L=L(t_0)$ . Integration performed in one time step  $dt=\tau$  over results in hundred time steps of  $\tau/100$ . Prescribed shape of P/L in time according to Figure 2 are used. The envelope of the results for every shape is shown, (V) for all shapes, (X) for shapes excluding “+/-“ cases and the concave cases.

**Figure 8.** Same as Figure 7 but using  $P=P(t_1)$  and  $L=L(t_1)$ .

**Figure 9.** Same as Figure 7 but using  $P=(P(t_0)+P(t_1))/2$  and  $P=P(t_1)$  for concave cases and for all others, respectively. (Same for L). For concave cases no PCE calculation is used but implicit steps for the entire range of  $dt>\tau/5$ .

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Vegetation Classes, 0.5x0.5 degrees (based on Olson NCAR-ds.769)

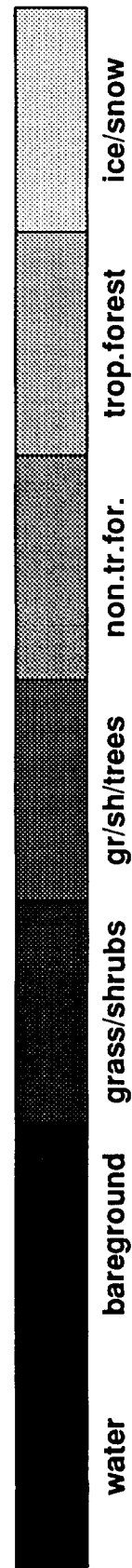


Fig 3

HNO<sub>3</sub> (JUL)-dep.-velocity, 2.8x2.8 deg (based on ds.769 & LARC snow/ice)

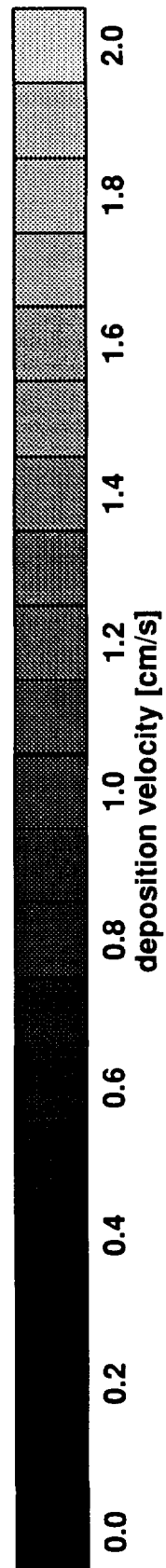
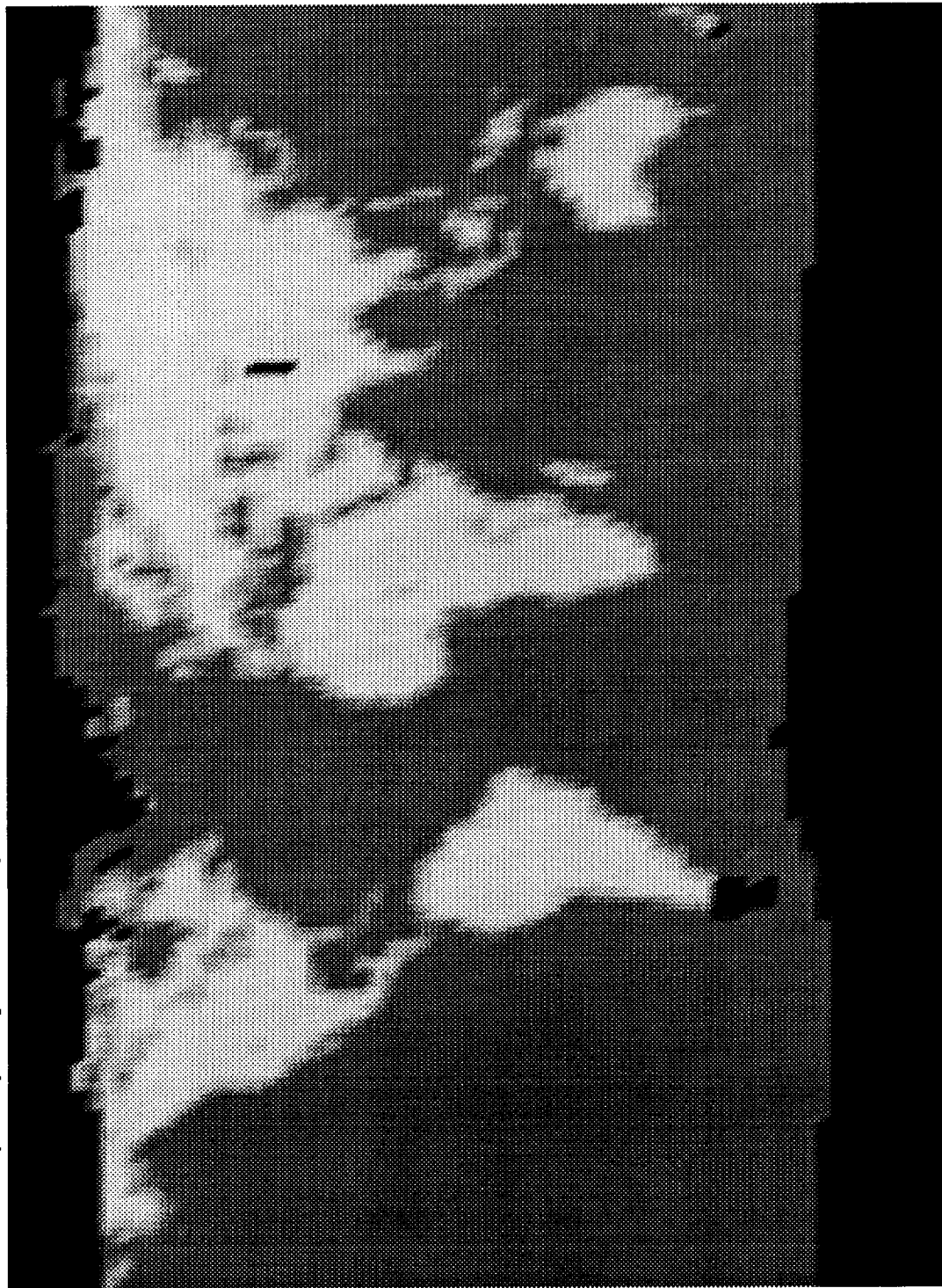
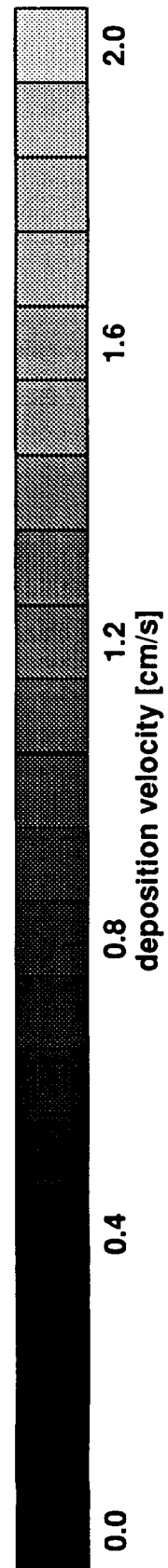
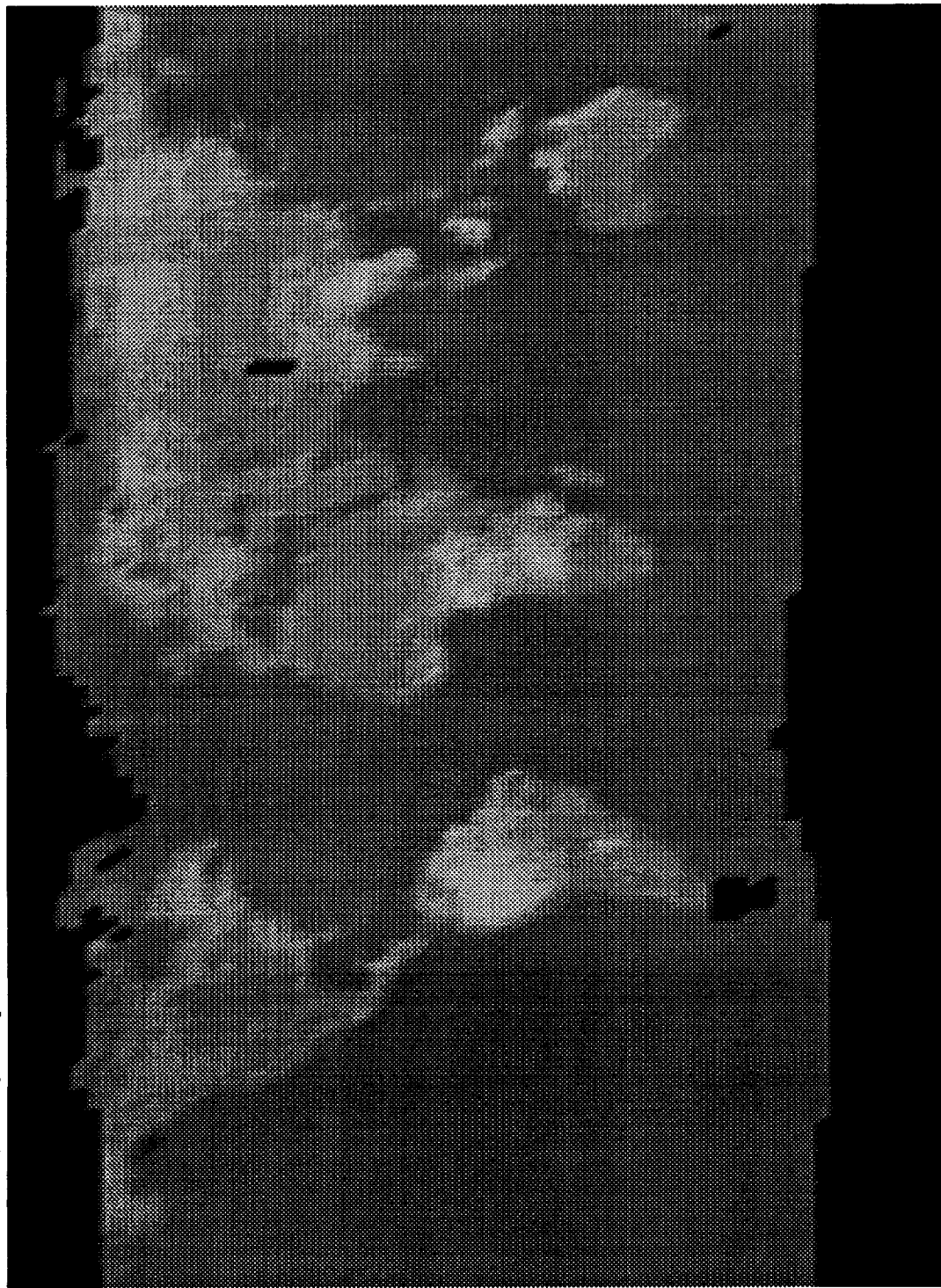


Fig 4a

H2O2 (JUL)-dep.-velocity, 2.8x2.8 deg (based on ds.769 & LARC snow/ice)



Ozone (JUL)-dep.-velocity, 2.8x2.8 deg (based on ds.769 & LARC snow/ice)

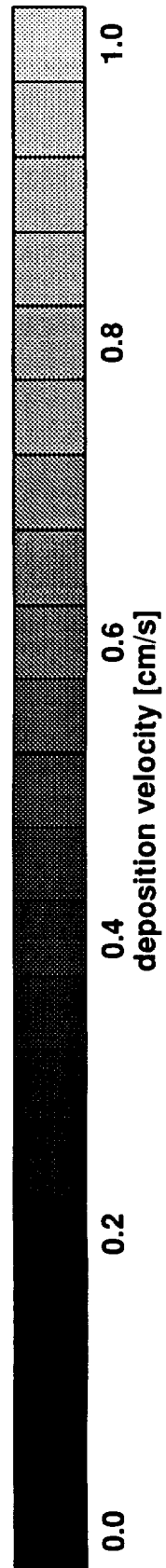
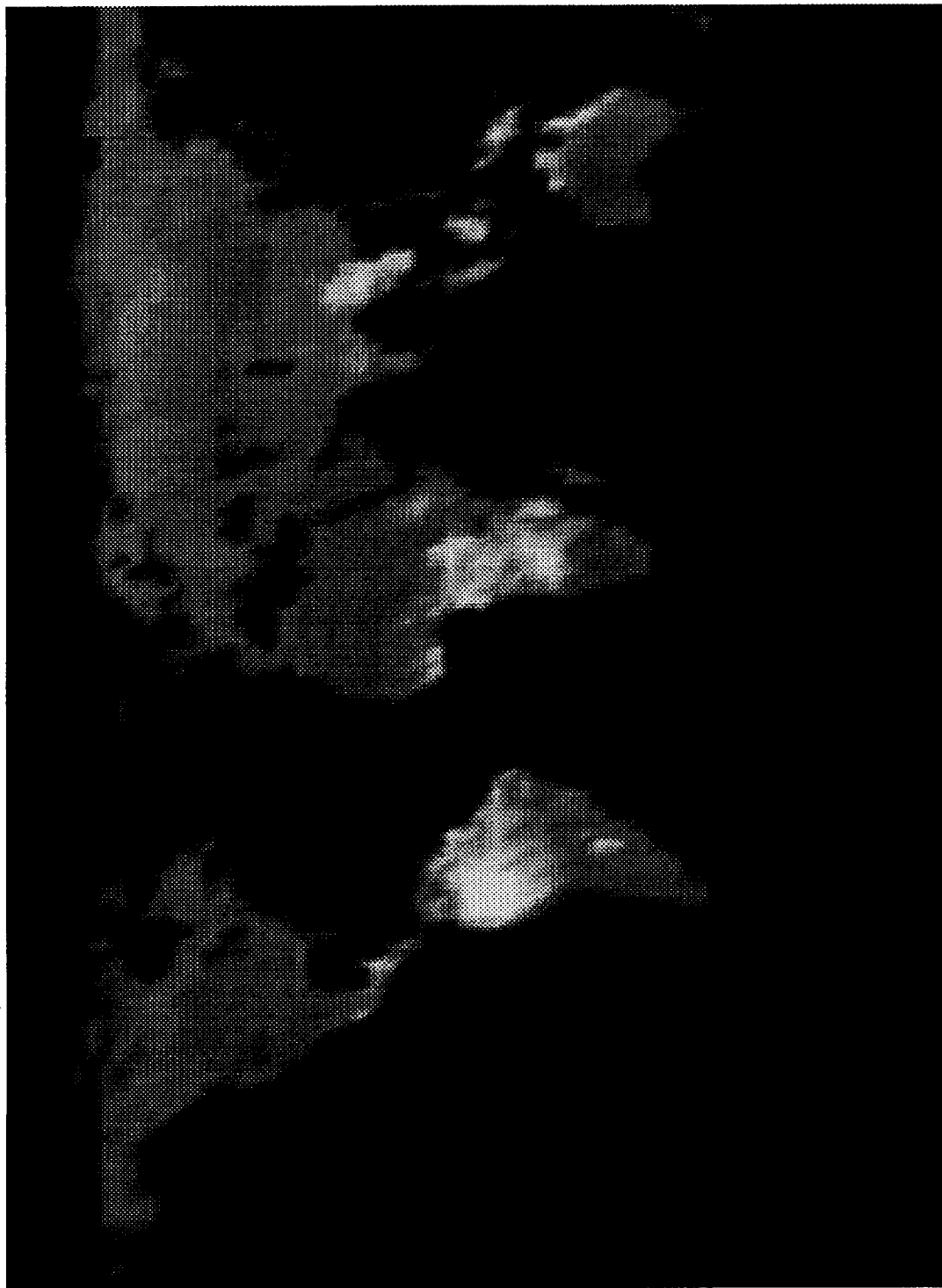


fig 4c



H<sub>2</sub>O<sub>2</sub> (pptv), Dec 25 Year 26 [Tr.Chem.] - [Trop.Chem.Ref.]

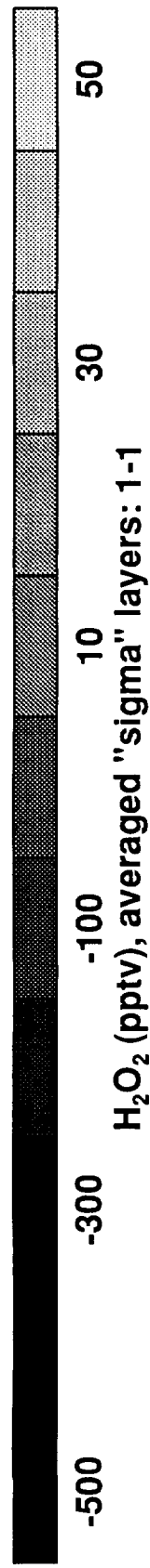
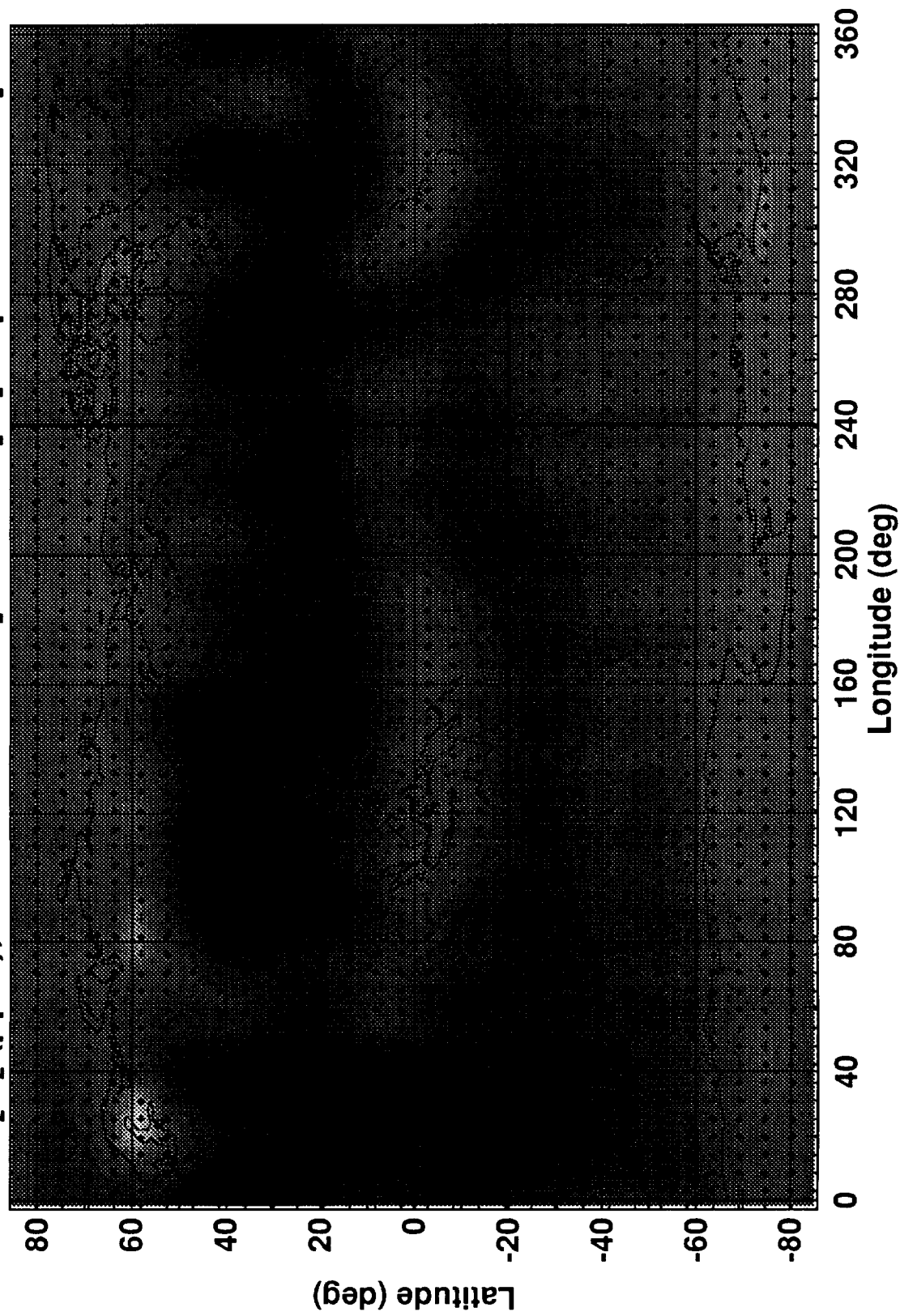


Fig 5a

O<sub>x</sub> (ppbv), Dec 25 Year 26 [Tr.Chem.] - [Trop.Chem.Ref.]

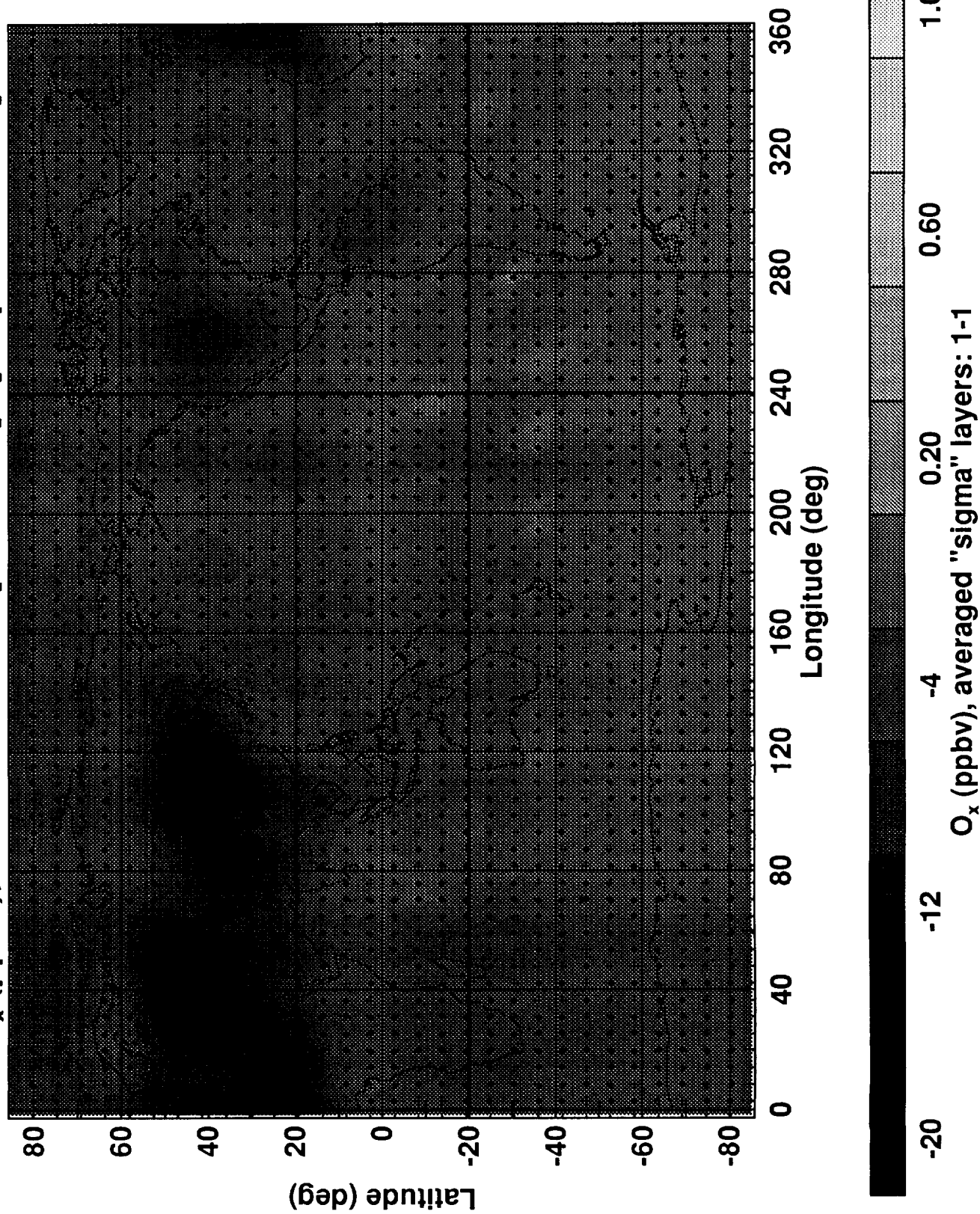
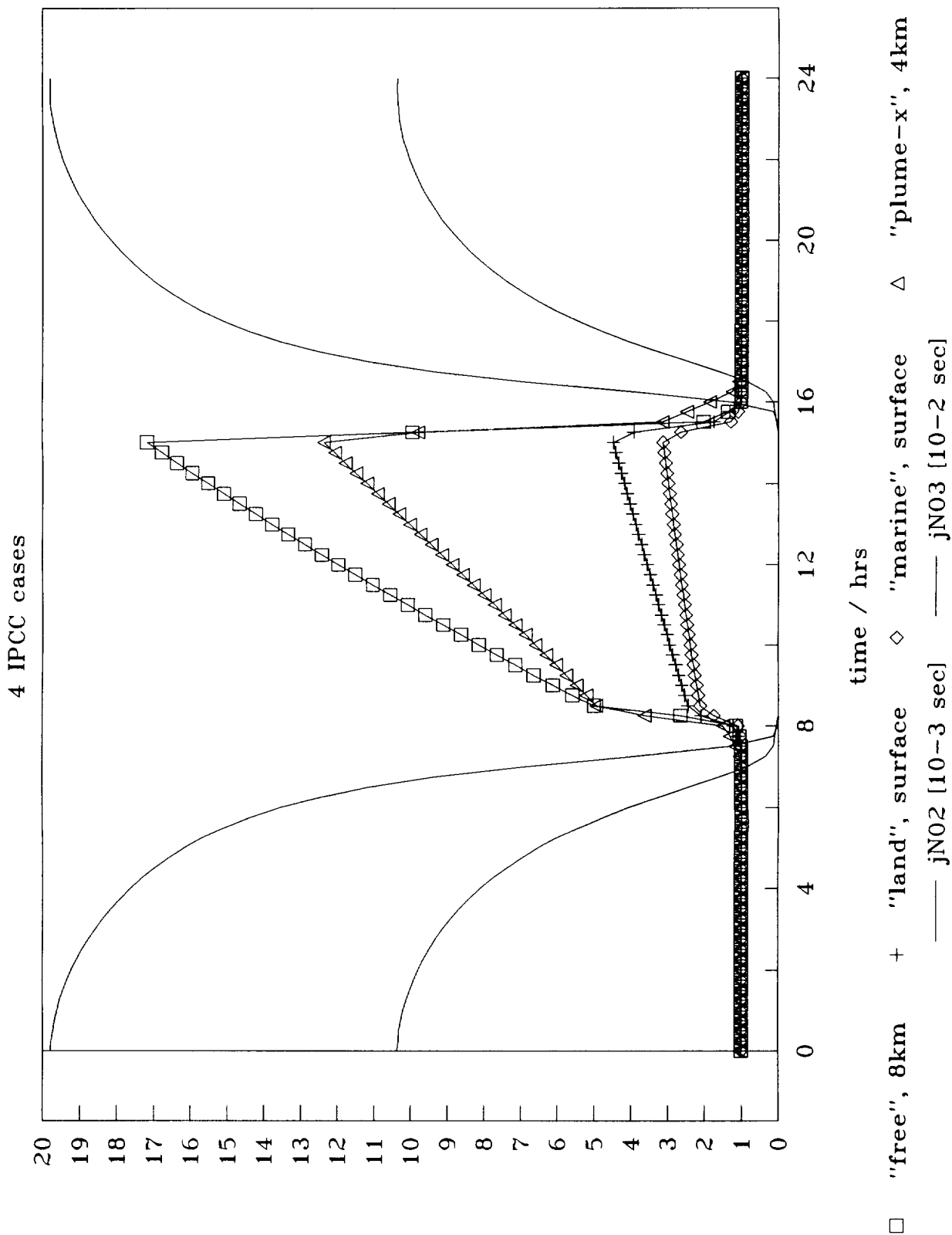
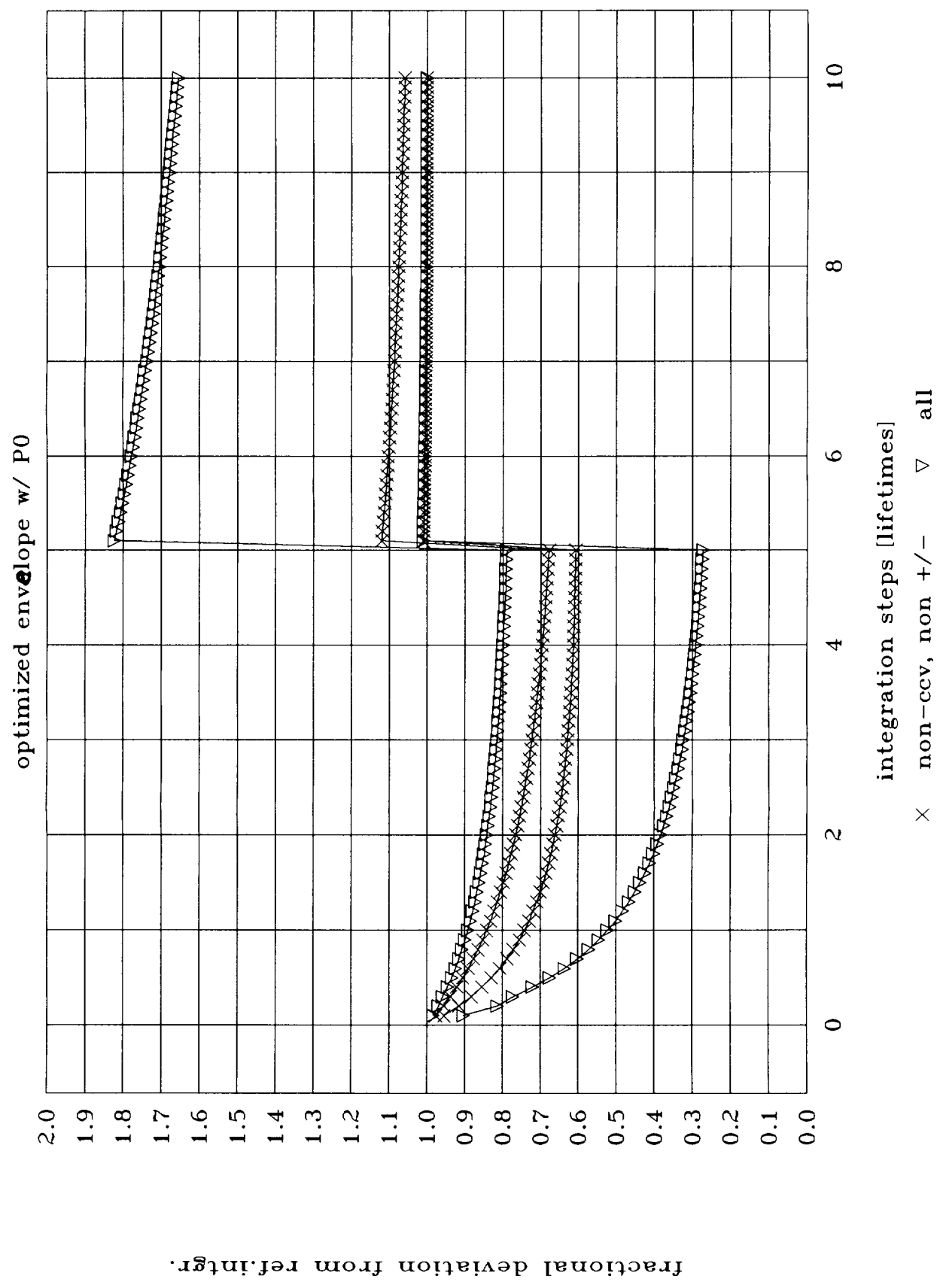


Fig 5b

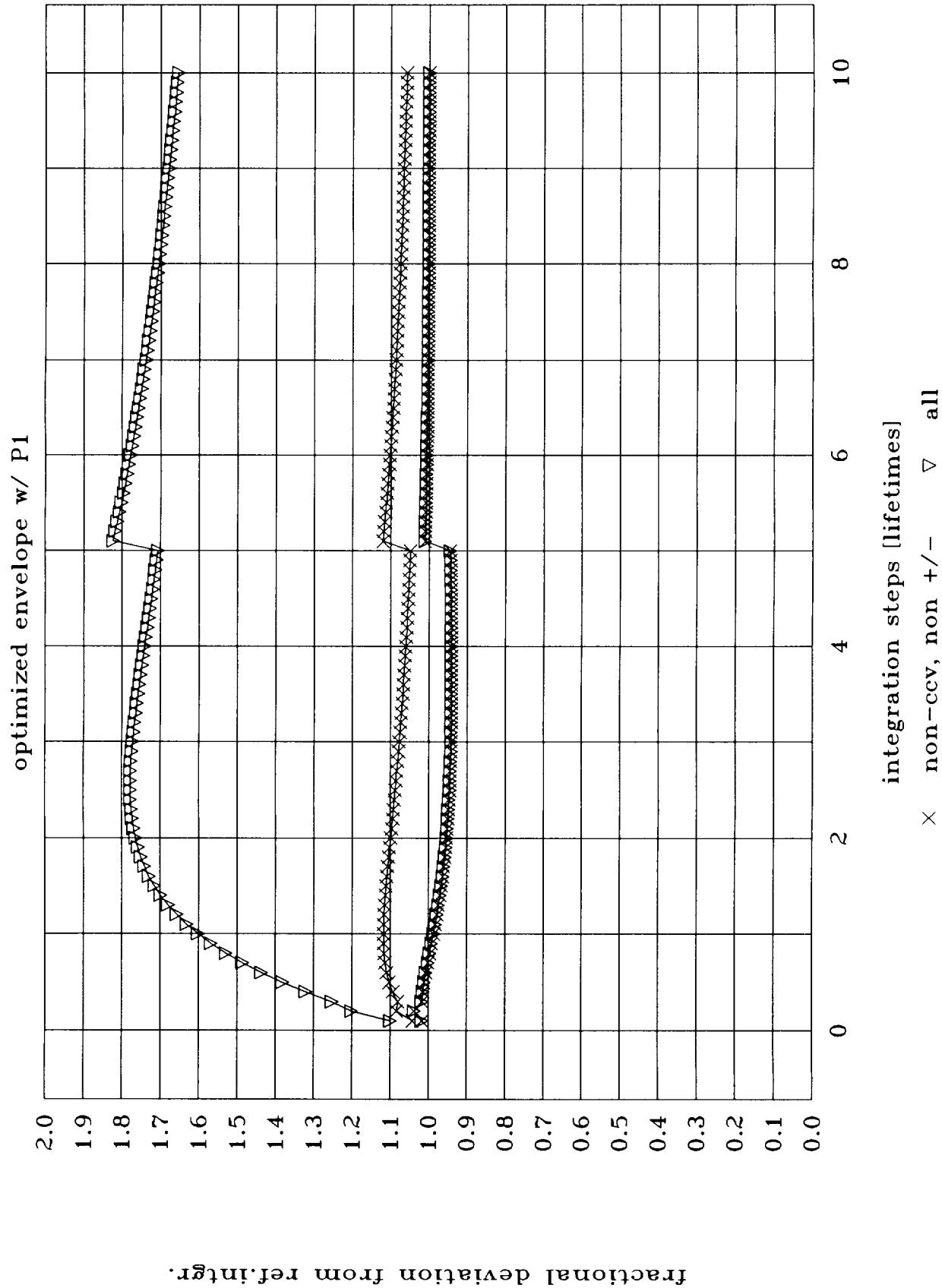
# Ratio of O3 loss rates: NO vs NOx added = $RL_{O_3}$



# Comparison of Integration Steps



# Comparison of Integration Steps



# Comparison of Integration Steps

optimized envelope w/  $P1 \leftrightarrow (P0+P1)/2$

